

The University of Chicago

A MOLECULAR REARRANGEMENT OF
PARA-PHENYLBENZBROMOAMIDE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1933

By

RACHEL FULLER BROWN

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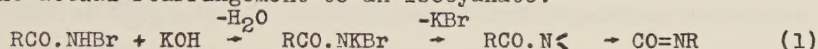
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THE MOLECULAR REARRANGEMENT OF
PARA-PHENYLBENZBROMOAMIDE¹

In the Hofmann rearrangement of an acylbromoamide RCO.NHBr by alkali the Stieglitz² theory assumes that an intermediate univalent nitrogen derivative RCO.N is first formed which undergoes the actual rearrangement to an isocyanate:



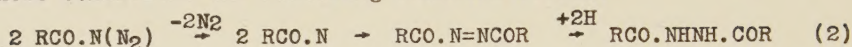
A great deal of evidence has been brought in support of this theory² which applies equally to the Lossen rearrangements of hydroxamic and dihydroxamic acids, the Beckmann rearrangement of oximes, the Curtius rearrangement of acyl azides and of analogous triaryl methyl derivatives studied by Stieglitz and his collaborators. Except in a single instance, no derivatives of the hypothetical univalent nitrogen intermediate compound have ever been observed other than rearrangement products involving the migration of R to N. The single instance of a derivative formed in which the grouping RCO.N remains intact is that of the formation of a diacylhydrazine RCO.NHNH.OCR in the reduction of an acyl azide as observed by Curtius.³ The product indicates that under

¹This investigation was completed in 1926. The submission of the dissertation and the publication of the results obtained have been delayed by the professional duties of the writer in the Division of Laboratories and Research, New York State Department of Health.

²Am. Chem. J., 15, 215 (1893); *ibid.*, 18, 751 (1896), etc. For the electronic formulation of the univalent nitrogen theory see Stieglitz and Leech, J. Am. Chem. Soc., 36, 272 (1914), Stieglitz and Stagner, *ibid.*, 38, 2046 (1911), and later reports by Stieglitz (e.g. Dohme Lecture, Johns Hopkins University, February, 1932). Cf. Lauder W. Jones, Am. Chem. J., 50, 441 (1913).

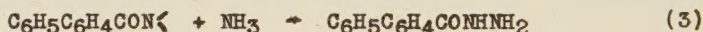
³Ber. d. chem. Ges., 27, 778 (1894); J. prakt. Chem., 50, 289 (1894).

these conditions the following reaction occurs:¹

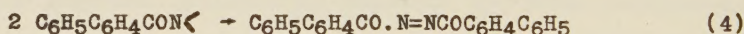


The present investigation was undertaken as an effort to secure further direct evidence of the intermediate existence of the univalent nitrogen compound $\text{RCO.N}\cdot$ by direct absorption by the univalent nitrogen. In an effort to slow up its normal tendency to rearrange at once, the diphenyl radical $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\cdot$ was selected and the behavior of paraphenylbenzobromoamide $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CONHBr}$ therefore studied. This choice was suggested by the increased stability as a free radicle of tri-diphenylmethyl $(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{C}\cdot$ as compared with triphenylmethyl $(\text{C}_6\text{H}_5)_3\text{C}\cdot$.

The addition of ammonia to the intermediate univalent nitrogen compound to form a hydrazide:

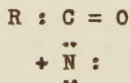


was tried but without success. An effort was then made to find an azo compound formed by direct combination of the two univalent nitrogen radicles:



But again the results were negative.

Evidently the intramolecular forces bringing about the rearrangement act too rapidly to afford opportunity for action between discrete molecules. One must bear in mind the fact that in a molecule of the electrical structure²

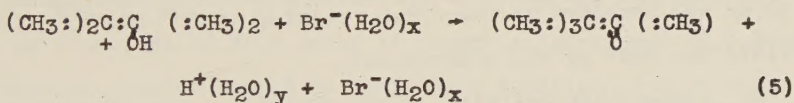


the attractive force of the free positive charge on the nitrogen atom acts within atomic distances on the electron doublet of the

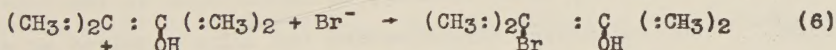
¹Stieglitz, Am. Chem. J., 18, 751 (1896).

²Only the essential charges are indicated.

group R:. The passage of R: to the positive charge on the nitrogen atom completes the rearrangement.¹ This interpretation finds support from observations made in this laboratory in the study of the pinacol rearrangement under the influence of halogen acids. There is a distinct difference in the action, on the one hand, of aqueous halogen acids producing hydrated ions, and of anhydrous acids, on the other hand, producing dry oxonium salts. When aqueous hydrogen bromide acts on pinacol, the oxonium ion first formed loses water and produces a carbonium ion; the positive charge of this ion is so close to :CH₃ groups that one of these slips to the positive charge before the comparatively distant bromide ion can combine with it to form an alkyl halide, which would be the product of the ordinary reaction of an alcohol with hydrogen bromide. In the rearrangement we have:



On the other hand, hydrogen bromide gas combines with pinacol in an inert solvent (e.g. benzene) to form an oxonium bromide, which left to itself in a desiccator goes over into the corresponding bromide:



In the experimental part the preparation of p-phenylbenz-bromoamide and of various derivatives is described and the experimental details are given for the main objective of the investigation.

EXPERIMENTAL PART

I. Preparative Methods

For the preparation of p-phenylbenz-bromoamide a start was

¹Cf. Stieglitz, loc. cit.

made from diphenyl. By nitration and subsequent reduction of nitro-diphenyl amino-diphenyl was obtained. By diazotization and a Sandmeyer reaction the amine was converted into p-phenylbenzonitril and from this the corresponding amid and bromoamid were obtained without difficulty.

Because of the meagre data in the literature regarding the preparation of these compounds a somewhat detailed description will be given here.

1. p-Nitrodiphenyl, $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_5$:-- For the preparation of p-nitrodiphenyl, Eastman's diphenyl was used. The method of Raiford¹ was followed, giving 49% of the theoretical yield of pure p-nitrodiphenyl melting at 113° .

2. p-Aminodiphenyl, $p\text{-H}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_5$:-- The best method for reducing p-nitrodiphenyl was found to be that of Schlenk.² The amine was obtained in pure form, melting at $52^\circ\text{--}52.5^\circ$.³ The yield was 94%⁴ of the theoretical.

3. p-Phenylbenzonitrile, $p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{CN}$:-- The nitrile was obtained with some difficulty by the diazotization of p-amino-diphenyl and a subsequent Sandmeyer reaction. Because of the great insolubility of p-aminodiphenyl hydrochloride the diazotization was found to be very slow, contrary to indications in the literature^{5,6} For successful diazotization the amine required an excess of acid, no doubt for the complete conversion of the base

¹Raiford and Colbert, Jour. Am. Chem. Soc., 47, 1454 (1925).

²Schlenk, Ann. 368, 295 (1909).

³Heusler, Ann. 260, 233 (1890) gives melting point as 53° ; Hofmann, Compt. Rend. 55, 901 (1862) as 45° ; Hübner, Ann. 209, 339 (1881) as $48\text{--}49^\circ$; Ostén, Ber. 7, 170 (1874) as $48\text{--}49^\circ$; and Schultz, Ann. 174, 201 (1874) as 49° .

⁴Schlenk reported a 72% yield.

⁵Ullmann, Ann. 332, 52 (1904).

⁶Kaiser, Ann. 257, 95 (1890).

into its hydrochloride. On the other hand, the excess of acid was detrimental to the Sandmeyer reactions. These difficulties were overcome by the following process:

For the preparation of the hydrochloride p-aminodiphenyl (15 g.) was ground with hydrochloric acid (26 c.c., sp. g. 1.26). The mixture was transferred to a flask containing 100 c.c. of water and warmed on the water bath for an hour. The mixture was next cooled with about 200 grams of crushed ice, and a solution of 7.5 grams of sodium nitrite dissolved in 200 c.c. of ice water was added slowly over a period of one hour. After the mixture had stood three and a half hours in an ice bath, the hydrochloride had gone almost completely into solution to form the diazonium salt. The excess of acid was neutralized with solid sodium carbonate. The p-aminodiphenyldiazonium chloride solution was filtered and added to a mixture of 24.3 grams of copper sulphate and 29.4 grams of potassium cyanide warmed to 90°. This addition took an hour and a half. The mixture was finally heated on a boiling water bath for 20 minutes, and then subjected to steam distillation. p-Phenylbenzonitrile passed over very slowly but in a pure state. The use of superheated steam gave a crude product which was not readily purified from alcohol. By this method it was possible to obtain 8.8 grams of pure p-phenylbenzonitrile melting at 86.5° to 87°. This was 55% of the theoretical yield.

4. p-Phenylbenzamide, $C_6H_5C_6H_4CONH_2$:-- The hydrolysis of p-phenylbenzonitrile to p-phenylbenzamide was found to take place readily when the nitrile (10 g.) was heated at 80°-90° for 16 hours with sulphuric acid (250 c.c.) containing 3 parts of sulphuric acid (sp. g. 1.84) and 2 parts of water by volume. A higher temperature resulted in sulphonation.¹ After the mixture

¹Rassow, Ann. 282, 139 (1894).

was cooled, diluted, and filtered, the precipitate was suspended in water and subjected to steam distillation; 0.5 g. of p-phenylbenzonitrile was thus recovered. The remaining precipitate was collected and recrystallized from alcohol and gave 8.4 g. of pure p-phenylbenzamide of melting point 225.5° - 226.5° .¹ This was 75% of the theoretical yield. p-Phenylbenzamide is readily soluble in glacial acetic acid, and slightly less soluble in benzene, chloroform, and ethyl acetate. It crystallizes from the last three solvents in needles, and from methyl and ethyl alcohols, in which it is only moderately soluble, it crystallizes in plates.

5. p-Phenylbenzoic acid, $C_6H_5C_6H_4COOH$:-- The hydrolysis of p-phenylbenzonitrile to p-phenylbenzoic acid was accomplished best by the use of alcoholic potash.² By recrystallization of the crude p-phenylbenzoic acid from alcohol, 65.5% of the theoretical yield of pure acid with a melting point of 221° ³ was obtained.

6. p-Phenylbenzoyl Chloride, $C_6H_5C_6H_4CO.Cl$:-- The method of Scholl and Seer⁴ for the preparation of p-phenylbenzoyl chloride from p-phenylbenzoic acid was used. The best yield obtained was 72% of the theoretical. The melting point was 113° .

7. p-Phenylbenzobromoamide, $C_6H_5C_6H_4CO.NHBr$:-- Because of the extreme insolubility of p-phenylbenzamide in dilute alkali, the usual methods for the preparation of bromoamides were not applicable.^{5,6} Good results, however, were obtained by following

¹Gattermann, Ber. 32, 1120 (1899) gives the melting point as 222° to 223° .

²Doebner, Ann. 172, 109 (1874).

³Doebner, loc. cit., gives the melting point as 218° - 219° ; Gattermann, loc. cit., as 218° ; Liebermann and Zsuffa, Ber. 44, 852 (1911) as 224° ; Rassow, loc. cit., as 218° ; Schlenk, loc. cit., as 222° ; and Schultz, loc. cit., as 216° - 217° .

⁴Scholl and Seer, Ann. 394, 148 (1912).

⁵Hofmann, Ber. 15, 407, 752 (1882).

⁶Hoogewerff and Van Dorp, Rec. Trav. Chim., 8, 173 (1889).

the method used by Chattaway and Orton¹ in the preparation of benz bromoanilide. A hot alcoholic solution of p-phenylbenzamide was added slowly to a cold solution which contained ten times the calculated amount of hypobromite. The hypobromite solution was made from one molecule of potassium hydroxide in a 10% aqueous solution and one molecule of bromine. During the addition of the p-phenylbenzamide solution to the hypobromite solution, the temperature was not allowed to rise above 0°. A small amount of unchanged p-phenylbenzamide separated out and was quickly removed by filtration. When the clear solution was acidified with cold 5% acetic acid, a heavy precipitate of p-phenylbenzbromoamide formed. This was collected quickly on a filter and dried on a clay plate in a vacuum desiccator over sulphuric acid and phosphorus pentoxide. The product thus obtained was a perfectly white powder.

Analysis for $C_{13}H_{10}ONBr$:

Active Br: Calcd. 28.96%

Found: 28.73%
28.88%

This almost pure product was obtained in 82% of the theoretical yield. Solution in chloroform and precipitation with ligroin gave fine white needles which, by analysis, were 100% pure. p-Phenylbenzbromoamide decomposes without melting at 138°. At ordinary temperatures it is stable. A sample which was kept 8 weeks in a brown desiccator gave the following analysis: active Br 29.09% and 29.08%. It is sparingly soluble in methyl and ethyl alcohols chloroform and benzene. It is little soluble in ether, less so in ligroin, and insoluble in water.

8. Potassium Salt of p-Phenylbenzbromoamide, $C_6H_5C_6H_4CONKBr$:--

¹Chattaway and Orton, Ber. 32, 3580 (1899).

Since p-phenylbenzbromoamide is almost insoluble in dilute alkali, the method used by Stieglitz and Eckstein¹ in this laboratory for preparing potassium salts of chloroamides could not be used. The potassium salt was readily prepared,² however, by the addition of a slight excess of potassium hydroxide, dissolved in absolute ethyl alcohol, to a dry ether solution of p-phenylbenzbromoamide kept at -15°. A white precipitate separated at once, was removed by filtration, washed thoroughly with cold dry ether, and dried as quickly as possible on a clay plate. The salt could be pressed to a dry white powder without explosion. As the dry salt spontaneously decomposed before a sample could be weighed in the ordinary ways, the analysis was carried out as follows: a sample of the freshly prepared dry salt was weighed into an acidified alcoholic potassium iodide solution; the solution was then titrated with thiosulphate solution.

Analysis for $C_{13}H_9ONBrK$:

Active Br: Calcd. 25.46%; found 25.28%

II. Molecular Rearrangement of p-Phenylbenzbromoamide

The rearrangement of the bromoamide was carried out by means of two reagents, (1) potassium hydroxide and (2) sodium ethylate.

1. Pure p-phenylbenzbromoamide (1 g.) was added slowly to a solution of potassium hydroxide (5 g.) in water (10 c.c.). The mixture was warmed slightly until it became reddish brown. A very faint odor of isocyanate was observed. After the mixture had cooled, the precipitate was collected on a filter and washed well with water. Extraction with ether and subsequent evaporation of the solvent in air gave 0.5 gram of p-amino-diphenyl which melted

¹Stieglitz and Eckstein, unpublished work, 1905.

²The yields ranged from 80-85% of the theoretical.

at 52°-52.5°. The chloroplatinate was prepared from the hydrochloride.

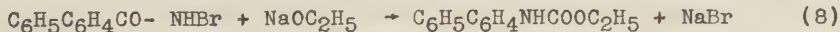
Analysis for $C_{24}H_{24}N_2PtCl_6$:

Pt: Calcd. 26.10%; found 26.14%

In this experiment, 81% of the p-phenylbenzbromoamide underwent rearrangement according to the following equation:



2. Pure p-phenylbenzbromoamide (0.5 g.) was warmed for 5 minutes on the water bath with an absolute ethyl alcohol (15 c.c.) solution of sodium ethylate prepared from 0.05 gram of sodium. The excess of alkali was neutralized with acetic acid and the alcohol removed by evaporation. A wax-like residue was collected on a filter, washed with water and dried on a clay plate. A yield of 0.45 gram of a faintly reddish material was obtained, melting at 107°-108°, close to the melting point, 110°, recorded for p-diphenylurethane. When a solution was made in warm ether and the solvent evaporated in the air, 0.25 gram of the urethane was obtained, melting at 110.5°-111.5°. Some of this urethane was hydrolyzed with hydrochloric acid. The product so obtained proved to be p-aminodiphenyl, since its melting point was 51° and its melting point when mixed with pure p-aminodiphenyl was 51°-52°. The formation of a urethane from any acyl bromoamide and sodium ethylate is a normal reaction:¹



In both of these experiments the rearrangement of p-phenylbenzbromoamide took place very readily.

III. Spontaneous Decomposition of the Potassium Salt of p-Phenylbenzbromoamide

Two organic substances could always be isolated in quantity

¹ Lengfeld and Stieglitz, Am. Chem. J., 15, 215 (1893), etc.

after the dry potassium salt of p-phenylbenzobromoamide had decomposed: the one was found to be p-aminodiphenyl and the other a urea which has not yet been further identified. Traces of a colored substance were also produced by the decomposition and this was later identified as azodiphenyl.

1. The potassium salt prepared from 2 grams of p-phenyl-benzobromoamide was allowed to decompose in the air. The resulting material gave no test for active bromine. It was extracted with dry ether and dry hydrogen chloride was passed through the ether solution to precipitate p-aminodiphenyl hydrochloride. The precipitate when collected and dried weighed 1 gram. It was identified by the analysis of its chloroplatinate:

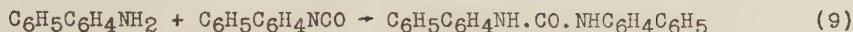
Analysis for $C_{24}H_{24}N_2PtCl_6$:

Pt: Calcd. 26.10%; found 26.04%.

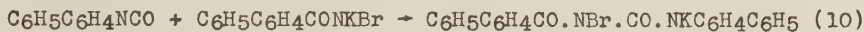
Some of the hydrochloride was treated with sodium hydroxide and the melting point of the p-aminodiphenyl thus formed was 52° - 53° .

2. The rearrangement products which had been insoluble in ether weighed 1 gram. They were washed with water to remove potassium bromide, leaving 0.3 gram of organic material. It melted at 285° - 292.5° . Recrystallized from glacial acetic acid it formed fine needles which melted at 293.5° with decomposition. The product was insoluble in dilute mineral acids, alkalies, water, alcohol, ether, xylene, toluene, and only very slightly soluble in boiling benzene. It was sparingly soluble in hot glacial acetic acid. This substance contained carbon, hydrogen, and nitrogen. It was probably one of two ureas: sym. di-biphenyl-urea, $C_6H_5C_6H_4NH.CO.NHC_6H_4C_6H_5$, or sym. p-phenylbenzoyl diphenyl-urea, $C_6H_5C_6H_4CO.NH.CO.NHC_6H_4C_6H_5$. It will be recalled that in the rearrangements of acyl bromoamides isocyanates are the first

identifiable products. Diphenyl isocyanate acting on aminodiphenyl would produce the symmetrical urea:



The action of the isocyanate on the potassium salt of the bromoamide before it had decomposed would give rise to the acylated urea:¹



Because of the absence of any active bromine after the rearrangement the symmetrical urea was at first considered the more probable product. It was, therefore, prepared by the action of phosgene on p-aminodiphenyl. To a solution of p-aminodiphenyl (4 g.) in benzene (30 c.c.) a 20% toluene solution (10 c.c.) of phosgene was added slowly. The precipitated urea was collected on a filter and washed with benzene and water. The crude material weighed 4.1 grams and melted at 298°. It was possible to recrystallize the urea from boiling water. The product so purified melted at 191°, resolidified immediately, and remelted at 299°.

Analysis: $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}$:

	C	H	N
Calcd.	82.38%	5.53%	7.69%
Found	82.19	5.57	7.78
	82.13	5.59	7.79

This sym.-di-biphenyl urea did not have the solubilities nor the melting point of the urea produced by the spontaneous decomposition of the potassium salt of p-phenylbenzobromoamide in the dry condition.

Melting points:

(a) sym.-di-biphenyl urea 191° and 299°

¹

Cf. Stieglitz and Earle, Am. Chem. J., 30, 412 (1903).

(b) rearrangement product	293.5°
(c) mixture of (a) and (b)	298°
(d) (b) seeded with (a) and allowed to stand 2 weeks	293.5°

Since the melting point 298° of the mixture of (a) and (b) showed only a very slight lowering from the melting point 299° of the pure, synthetic urea, the two might very well be identical. However, their general behavior (solubilities and the absence of a double melting point in the rearrangement product) left a doubt as to their identity. On the other hand when the rearrangement was carried out in a benzene suspension of the potassium salt in the presence of anhydrous ammonia, sym.-di-biphenylurea ($\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{NH}$)₂CO was obtained and positively identified by its double melting point (191° and 299°) and its other characteristics (see page 15).

3. The identification of the colored substance formed in the decomposition of the potassium salt of p-phenylbenzbromoamide was next accomplished. The salt, prepared from 2 grams of p-phenylbenzbromoamide, was put into cold benzene which was allowed to come gradually to room temperature. The benzene solution became yellow in color. The insoluble urea and potassium bromide were removed by filtration. The benzene solution was evaporated to dryness in a vacuum desiccator and the residue taken up in dry ether. The hydrochloride of p-aminodiphenyl was precipitated by dry hydrogen chloride and removed by filtration. The orange colored ether filtrate was then concentrated in a vacuum desiccator. Before the ether had been completely removed a small crop of orange plates separated. These were collected on a filter and washed with cold ether. This material formed a deep purple color in contact with concentrated sulphuric acid. Its melting point was 248.5°. The melting point of a mixture of the substance with

some synthetic azodiphenyl melting at 251.5°-252.5° was 250.5°-251.5°. The orange substance was, therefore, azodiphenyl, $C_6H_5C_6H_4N=NC_6H_4C_6H_5$. It may have been produced by the action of active bromine on p-aminodiphenyl formed in the rearrangement of the potassium salt of p-phenyl-benzbromoamide. Since azodiphenyl is formed in this decomposition, some product besides those isolated must be formed in traces. If the potassium salt of p-phenyl-benzbromoamide oxidized the p-aminodiphenyl, p-phenylbenzamide should be formed in traces. Or, the formation of an acyl-aryl urea would account for the oxidation, since hypobromite is released in the action. (See equations 10 and 11.)

In order to confirm the belief that the p-aminodiphenyl had been oxidized by active bromine, the action of potassium hypobromite on p-aminodiphenyl was investigated.^{1,2} A hypobromite solution was made from 4 grams of potassium hydroxide and 2 grams of bromine in 20 c.c. of water. One-half the calculated amount of this solution (5 c.c.) was added to a cold ether solution of 1 gram of p-aminodiphenyl. When the mixture was shaken, the ether layer at once showed a deep orange color. This mixture was left in the ice box $2\frac{1}{2}$ days. The orange deposit which formed was collected on a filter and washed with ether. This crude product melted at 242°. When recrystallized from ether the melting point was 251.5°-252.5°. The melting point of azodiphenyl has been reported as 249°-250°.³ The yield was 0.1 gram. The recrystallized product formed in microscopic plates similar to those observed in the previous experiment.

¹This experiment could probably be repeated to give a quantitative yield of azodiphenyl.

²For the action of hypobromite solutions on primary amines see Meigen and Nottebohm, Ber. 39, 744 (1906).

³Zimmerman, Ber. 13, 1962 (1880).

IV. Attempts to Obtain Evidence for a Univalent Nitrogen Compound
 $C_6H_5C_6H_4CO.N\angle$ as an Intermediate Product in the Rearrangement of
the Potassium Salt of p-Phenylbenzbromoamide

1. A stream of dry ammonia was passed through a benzene suspension of the potassium salt of p-phenylbenzbromoamide. To hasten the decomposition the temperature of the mixture was raised to the boiling point of benzene. p-Phenylhydrazide would be the product of the reaction if the univalent nitrogen compound absorbed ammonia at the free valences of the univalent nitrogen:



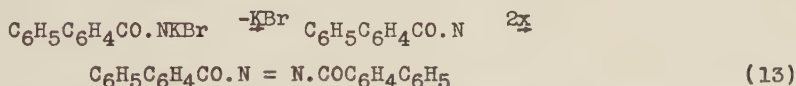
In order to study the properties of p-phenylbenzhydrazide, it was prepared from p-phenylbenzoyl chloride and hydrazine hydrate: a solution of the chloride (1.5 g.) in ether (100 c.c.) was added gradually to a 50% solution of hydrazine hydrate (6 g.). The mixture was shaken well during the addition. A heavy white curd formed at once. The ether was removed by evaporation on a water bath and the precipitate collected. It was dissolved in boiling water, and the hot solution was filtered at once from a slight residue of sym.-di-p-phenylbenzhydrazide. When the solution cooled, the p-phenylbenzhydrazide separated in fine needles. The melting point was 196°-197°. The yield was 0.9 gram or 63% of the theoretical. The hydrazide reduced Fehling's solution. (An analysis has not been made.)

In working up the reaction mixture from the decomposition of the potassium salt of p-phenylbenzbromoamide in the presence of ammonia, the yellow benzene solution was filtered. The solid residue was washed first with benzene and then with boiling water to dissolve any possible p-phenylbenzhydrazide. All but a trace, which could not be removed from the filter paper, went into solution. The precipitate which separated on cooling was collected

on a filter and washed with water. It melted at 191°, resolidified immediately, and remelted at 299° with decomposition. When mixed with sym.-di-biphenyl urea it had the same melting point. From 1.5 grams of the potassium salt of p-phenylbenzobromoamide 0.5 gram of the urea was obtained. In this case the urea formed in the rearrangement had the same properties as that prepared from p-aminodiphenyl and phosgene, and was undoubtedly sym.-di-biphenyl urea.

No trace of p-phenylbenzoylhydrazide was found in the reaction products.

2. When the colored substance formed in the decomposition of the potassium salt of p-phenylbenzobromoamide was first investigated it was thought that it might be azo-p-phenylbenzoyl which might be formed as follows:



The attempt was, therefore, made to prepare this compound. The method of Gilbert¹ for preparing sym-dibenzoylhydrazine was used to prepare sym-di-p-phenylbenzoylhydrazine. Pure material in 85% of the theoretical yield was obtained, melting at 286°. It was practically insoluble in all the common solvents except glacial acetic acid which was used for its purification.

Analysis for $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$:

	C	H	N
Calcd.	79.56%	5.14%	7.14%
Found	79.61 79.57	5.34 5.33	7.24 7.16

According to Stolle² the best method for oxidizing an

¹Gilbert, Abstracts of Theses, University of Chicago, Science Series, I, 177 (1922-3).

²Stolle, Ber. 45, 276 (1912).

acylhydrazine is to prepare its sodium salt, convert the latter into the mercury salt, and then to oxidize this salt with bromine.

When sym-di-p-phenylbenzoylhydrazine was suspended in alcohol and treated with two molecules of sodium ethylate, a yellow salt was formed at once. Analysis showed it to be the mono-sodium salt.

Analysis for $(C_{26}H_{19}O_2N_2)Na$:

Na: Calcd. 5.55%

Found 5.49
5.47

Neither the use of heat nor a large excess of sodium ethylate gave the di-sodium salt.

The sodium salt of sym-di-p-phenylbenzoylhydrazine was too insoluble in alcohol to make a solution. Therefore an alcoholic suspension was refluxed 15 hours with an excess of mercuric chloride. The yellow color of the precipitate faded considerably but not completely.

Analysis for $(C_{26}H_{18}O_2N_2)Hg$:

Hg: Calcd. 33.90%

Found 30.72

An attempt to mercurate in acetic acid solution failed entirely. A compound containing mercury has been prepared by stirring mechanically for 6 hours a warm 50% alcoholic suspension of the sodium salt with an excess of mercuric chloride. This has not been analyzed.

An attempt to oxidize the impure mercury salt by having it shaken in ether suspension with bromine for a day gave no colored product. Another attempt to oxidize the hydrazine itself by having it shaken in ether suspension with mercuric oxide and bromine for a day also gave no colored product.

The results up to the present indicate that azo-p-phenyl-

benzoyl cannot be prepared readily.

SUMMARY

1. p-Phenylbenzbromoamide and its potassium salt were prepared and their molecular rearrangements were studied. p-Phenylbenzbromoamide, with aqueous alkali, gave an 81% yield of p-aminodiphenyl; with an alcoholic solution of sodium ethylate it gave smoothly p-diphenylurethane. These are the normal rearrangement products.

2. Potassium p-phenylbenzbromoamide was found to undergo rearrangement spontaneously at room temperature, both in the dry condition and in a suspension in benzene. Besides p-aminodiphenyl the following products were identified: sym. di-biphenylurea, $(C_6H_5C_6H_4NH)_2CO$ and azodiphenyl, $C_6H_5C_6H_4N=NC_6H_4C_6H_5$. It was shown that azodiphenyl is formed by the oxidation of p-ammo-diphenyl by hypobromites.

3. Efforts were made to obtain direct evidence of the formation, in the course of the rearrangements, of an intermediate univalent nitrogen derivative $C_6H_5C_6H_4CO.N$ as postulated by the Stieglitz theory, by attempted additions to the univalent nitrogen before a Hofmann rearrangement intervened. The addition of ammonia to produce p-phenylbenzoylhydrazide, $C_6H_5C_6H_4CO.NHNH_2$, was tried but only the normal products of rearrangement were obtained. The conclusion was drawn that the intramolecular rearrangement is so fast that no opportunity for an intermolecular action with ammonia is afforded.

4. Evidence of the union of two molecular univalent nitrogen residues to form azo-p-phenylbenzoyl, $C_6H_5C_6H_4CON:NCOC_6H_4C_6H_5$ was next sought for. A critical examination of the reaction products gave a negative result, only the normal rearrangement products being formed. The same conclusion was drawn as in the preceding

case.

5. The exact conditions for the preparation of p-phenylbenzonitrile by the Sandmeyer reaction with a satisfactory yield were determined.

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